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X-Ray Fluorescence Analysis of Superalloy Leach Liquors Using a Thin-Film Technique

By R. D. Govier

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR



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of Superalloy Leach Liquors
Using a Thin-Film Technique**

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	μL	microliter
c/s	count per second	mA	milliampere
g/L	gram per liter	mL	milliliter
in	inch	mm	millimeter
kV	kilovolt	min	minute
μg	microgram	pct	percent
$\mu\text{g}/\text{cm}^2$	microgram per square centimeter	s	second

X-RAY FLUORESCENCE ANALYSIS OF SUPERALLOY LEACH LIQUORS USING A THIN-FILM TECHNIQUE

By R. D. Govier¹

ABSTRACT

The U.S. Bureau of Mines has developed a thin-film X-ray fluorescence technique to rapidly determine Cu, Ni, Co, Fe, and Cr in superalloy leach liquors. Total analysis time per sample was less than 15 min, as opposed to several hours for traditional wet chemical methods. Precision and accuracy were checked by replicate analyses of solutions similar in composition to leach liquors, whose analyte concentrations were well known. Coefficients of variation for all elements were found to be less than 2 pct. With the exception of the results for Fe, all relative errors of estimation were also found to be less than 2 pct. Bulk liquids are not introduced into the spectrometer; thus, the potential for damage to the instrument by leakage of corrosive liquids is eliminated.

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INTRODUCTION

Chromium, nickel, and cobalt are essential to the production of high-temperature, high-strength alloys used in applications such as jet engines. The United States is dependent on foreign sources for these metals because of their limited domestic availability. Research on recovery of these critical metals from superalloy scrap is currently under way at the U.S. Bureau of Mines, as part of its program to reduce U.S. dependence on foreign supplies by ensuring adequate domestic supplies of strategic minerals and metals.

One approach to the recovery of these critical metals involves the use of matte smelting techniques. In research at the Bureau, synthetic superalloy scrap was mixed with sulfur and smelted to form a matte. This matte was leached with a mixture of hydrochloric acid (HCl), cupric chloride, and chlorine gas, producing a leach liquor and a leach residue. The majority of the Ni, Co, and Fe, along with some Cr and W, was removed from the matte in this leaching step. Process efficacy was gauged by the analysis of leach liquor and leach residue.

Leach liquors were analyzed for 11 elements. Aluminum, molybdenum, niobium (columbium), tantalum, titanium, and tungsten were present in concentrations sufficiently low for easy analysis by inductively coupled plasma (ICP) emission spectrometry. Copper, nickel, cobalt, iron, and chromium were initially determined by traditional wet chemical methods because they were present in high concentrations. It was determined that the dilutions associated with the use of ICP or atomic absorption methods in the determination of these analytes could result in the introduction of large errors into the analysis. The labor-intensive nature of these wet methods and high concentrations of the analytes led to the exploration of X-ray fluorescence (XRF) techniques as a cost-effective alternative. Nickel was present in some samples at levels greater than 100 g/L. Copper could be found at levels above 50 g/L, Fe and Co above 10 g/L, and Cr above 3 g/L. A thin-film XRF technique was chosen to ensure the absence of absorption and enhancement (interelement) effects that might be present at these analyte levels in a bulk liquid sample.

The absence of substantial interelement effects in samples that have the form of thin films has been

demonstrated experimentally by Rhodin.² He found the absence of interelement effects in samples whose surface densities ranged from 1 to 100 $\mu\text{g}/\text{cm}^2$. Subsequently, Birks demonstrated theoretically that in samples of limited thickness analyte intensity is related simply to quantity and is not affected by matrix composition.³

In the method described here, thin-film specimens are produced from bulk leach liquors in a two-step process. Leach liquors are initially diluted 1:4 using volumetric pipets. An aliquot of the diluted leach liquor is then dispersed onto a filter paper circle. Thus, a thin-film specimen might contain up to 250 μg of analytes per square centimeter. Calibration curves for all analytes, prepared using the above method were linear, demonstrating the absence of interelement effects. The absence of interelement effects in specimens prepared by this method was further demonstrated using solutions containing only two analytes. Copper and cobalt could be expected to have large effects upon one another in the bulk; therefore, binary solutions were prepared from these elements. The Co concentration was held constant while Cu concentration was widely varied. No substantial interelement interferences for these two analytes were found. The absence of interelement effects for the other analytes can be inferred by analogy. Calibration curves prepared using bulk liquids showed substantial deviation from linearity, indicating the presence of interelement effects. Methods that can correct for interelement effects exist; however, they add complexity to the analytical scheme, increase the potential for error, and require larger numbers of standards. The method presented here is quick and simple, and requires few standards, which can be easily prepared. A further benefit of this method is that potential instrument damage from the leakage of bulk corrosive liquids is completely avoided. Most important, this method is both precise and accurate over wide analyte concentration ranges.

²Rhodin, T. N. Chemical Analysis of Thin Films by X-Ray Emission Spectrography. *Anal. Chem.*, v. 27, 1955, pp. 1857-1861.

³Birks, L. S. X-Ray Spectrochemical Analysis. Interscience Publ., 1959, 63 pp.

EXPERIMENTAL

EQUIPMENT

The equipment used was as follows:

1. Automated X-ray wavelength spectrometer system with tungsten X-ray tube and lithium fluoride 200 analyzing crystal.
2. Disposable sample cells, 31 mm.
3. Polyester film, 0.00025 in thick.
4. Filter paper circles, 2.1 cm diam.
5. Ultra-high-purity helium gas.
6. Proportional counting gas, 10 pct CH₄, 90 pct Ar.
7. Serological capillary tubes, 20 μ L.

SOLUTION PREPARATION

Four different types of solutions were prepared for this analysis. Standard solutions prepared from the metals were used to calibrate the spectrometer. Tests solutions were prepared from alloys of well-known composition to verify spectrometer calibration. The test solutions were not actual leach liquor samples. Binary solutions of two of the analyte metals, Cu and Co, were prepared to confirm the absence of interelement interferences. Leach liquor samples also required preparation to produce thin-film specimens from them.

Standard Solution Preparation

Four standards, each containing the five analytes, were prepared. Analyte concentrations were chosen to span the range expected in the leach liquor samples. Standard solution analyte concentrations are listed in table 1. One hundred milliliters of each standard was prepared from the high-purity metals by accurate weighing and dissolution with approximately 5 mL of nitric acid (HNO₃) and 20 mL of HCl in glass beakers. Beaker contents were transferred to volumetric flasks and diluted to volume. Thin-film specimens to be used for instrument calibration were prepared from these standard solutions in a two-step process. Standard solutions were initially diluted 1:4 by mixing a 5-mL aliquot of the standard with a 15-mL aliquot of water in a small plastic sample bottle. Twenty microliters of the standard was drawn into the serological capillary. The liquid was transferred onto a 2.1-cm filter paper circle that was lying on a sheet of polyester film twice as long as it was wide. The filter paper circle was held stationary with

a fingernail at the edge of the paper. Liquid was transferred by touching the tip of the capillary to the center of the paper and then moving it in an outwardly spiraling motion as the liquid wicked out onto the paper. The polyester film sheet was folded over the filter paper so that the filter paper was sandwiched between two polyester film layers. This sandwich was then mounted on a 31-mm sample cell. The use of a 20- μ L aliquot in conjunction with a 2.1-cm filter paper resulted in a specimen in which the sample liquid was homogeneously distributed throughout the filter paper. Acid attack of the filter papers was not a problem. Care was taken to ensure that filter circles were centered on the sample cells. A small pinhole was placed in the top polyester film layer to relieve any pressure between the layers that might cause bulging of the film. Sample cells were vented to ensure that pressure was not built up inside the cell during analysis. Pressure buildup could cause the specimen to bulge out in the center, introducing errors in the analytical result. This bulging was observed in specimens that were not vented.

Table 1.—Standard solution analyte concentrations, grams per liter

Standard	Cu	Ni	Co	Fe	Cr
1	3.84	79.06	11.95	5.13	0.11
2	14.19	41.32	1.02	3.51	.41
3	26.16	20.67	2.99	1.18	1.36
4	45.56	58.73	6.27	9.76	3.31

Test Solution Preparation

Test solutions of well-known analyte concentration were prepared in order to check the precision and accuracy of the method. These solutions were prepared from standard reference materials (SRM's) available from the National Bureau of Standards (NBS) and the same high-purity Ni used to prepare the standard solutions. The SRM's used were NBS 162A, Ni-Cu alloy, and NBS 349, heat-resisting alloy. Four stock solutions were prepared from the two SRM's and the high-purity Ni by dissolution with HCl and HNO₃:

<i>Solution</i>	
1	25.00 g/L NBS 349
2	25.00 g/L NBS 162A
3	50.00 g/L NBS 162A
4	24.98 g/L Ni

Aliquots of these stock solutions were mixed together to obtain test solutions whose analyte concentrations approximated those of the actual leach liquors to be analyzed. Test solution 1 was prepared by mixing one part stock solution 1 with one part water. Test solution 2 was prepared by mixing one part stock solution 1 with two parts stock solution 2. Test solution 3 was stock solution 2 without any treatment, and test solution 4 was prepared by mixing one part stock solution 1 with two parts stock solution 2 and three parts stock solution 4. Test solution analyte concentrations are presented in table 2.

In order to shorten the time necessary for the dissolution of the SRM's or high-purity Ni during the production of the stock solutions, only one-quarter of the actual required amount of SRM or Ni was dissolved. When thin-film specimens were prepared from the test solutions they were not diluted 1:4 as were the standards and samples; thus, the results of the analysis should be exactly four times that of the actual concentration. This procedure resulted in thin-film specimens of the test solutions whose analyte concentration ranges fell within that of the standards. Replicates of these test solutions were analyzed in order to obtain precision and accuracy data.

Table 2.—Test solution analyte concentrations, grams per liter

Solution	Cu	Ni	Co	Fe	Cr
1	(¹)	28.58	6.98	(¹)	9.90
2	20.42	61.69	4.70	1.50	6.54
3	30.61	63.95	(¹)	2.19	(¹)
4	20.41	102.1	2.38	1.48	3.28

¹Concentration below standard range.

Binary Solution Preparation

Binary solutions were prepared to confirm the absence of interelement interferences at analyte concentrations found in leach liquors. These solutions were prepared by accurately weighing the analyte metals Cu and Co into glass volumetric flasks and dissolving using HCl and HNO₃. As in the test solutions, only one-quarter of the actual required amount of metal was used. Thin-film specimens were prepared from these solutions in the same way as the standards, with the exception of the dilution step.

Sample Preparation

Sample solutions were treated in the same way as the standards to obtain thin-film specimens from them. No

attempt was made to match the standard and sample matrices exactly. Aluminum, molybdenum, niobium, tantalum, titanium, and tungsten could be present in the sample leach liquors in concentrations up to several grams per liter total. Chloride content varied between samples and standards also. It was believed at the outset that these factors would not have a significant influence on analytical results. This belief was validated when test solutions were subsequently analyzed.

ANALYTICAL PROCEDURE

Thin-film specimens of standards, leach liquors, test solutions, and binary solutions were prepared as outlined in the previous section. All intensity data were collected using a tungsten target X-ray tube operating at 35 kV and 20 mA. First-order K- α lines of each analyte were measured using a lithium fluoride 200 analyzing crystal and scintillation and flow proportional counters in a helium atmosphere. Pulse height analysis was used. The sample spinner was used to compensate for any inhomogenous dispersion of the sample liquids throughout the filter paper circles. Counting times for Ni, Fe, and Cr were 30 s at the peak and 10 s at the background. Copper and cobalt were counted for 60 s at the peak and 20 s at the background. With the exception of Cu, background count rates were derived by counting at an angle that was slightly greater than the angle of the peak. These backgrounds were assumed to be constant. The Cu peak, however, was overlapped by a scattered tube target line. In order to correct for this overlap, a sloping background correction was applied. The instrument was calibrated by applying a linear least squares curve-fitting technique to net intensity versus concentration data collected from two replicates of each standard. All subsequent analyses were accomplished using this initial instrument calibration. Calibration curves for all analytes are presented in figures 1 through 5.

Bulk solution calibration curve data were collected from a single 2-mL sample of each standard. Standard solutions were not diluted as they were for the thin-film specimens. The same analytical conditions were used for both bulk and thin-film specimens.

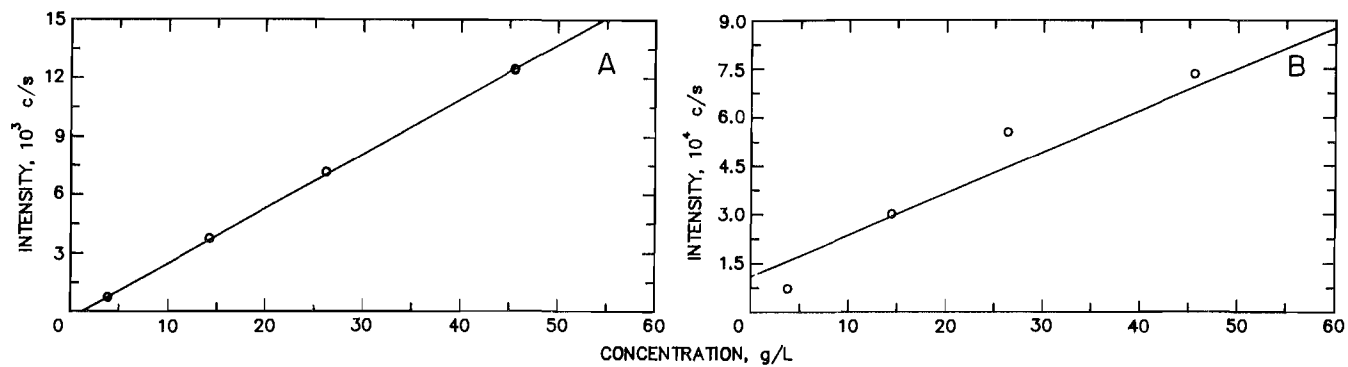


Figure 1.-Copper calibration curves. A, Thin film; B, bulk solution.

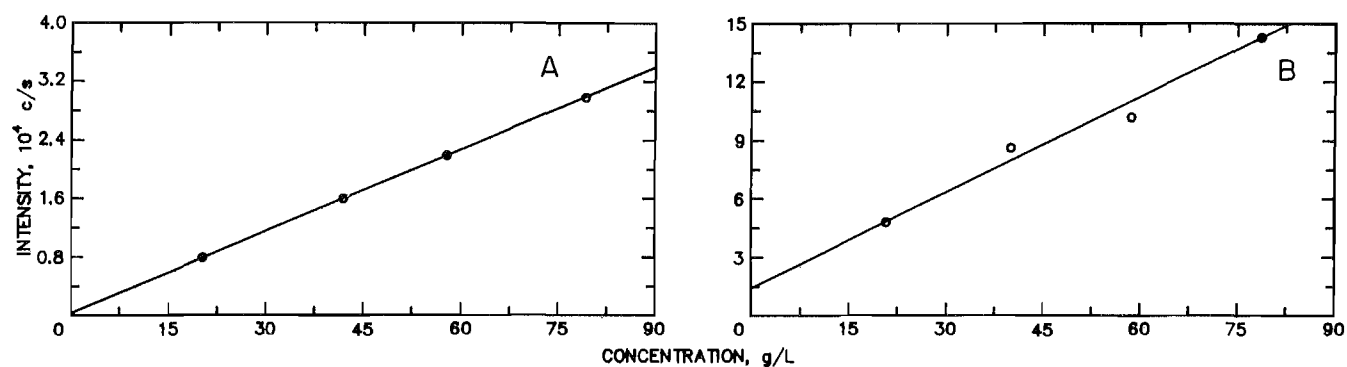


Figure 2.-Nickel calibration curves. A, Thin film; B, bulk solution.

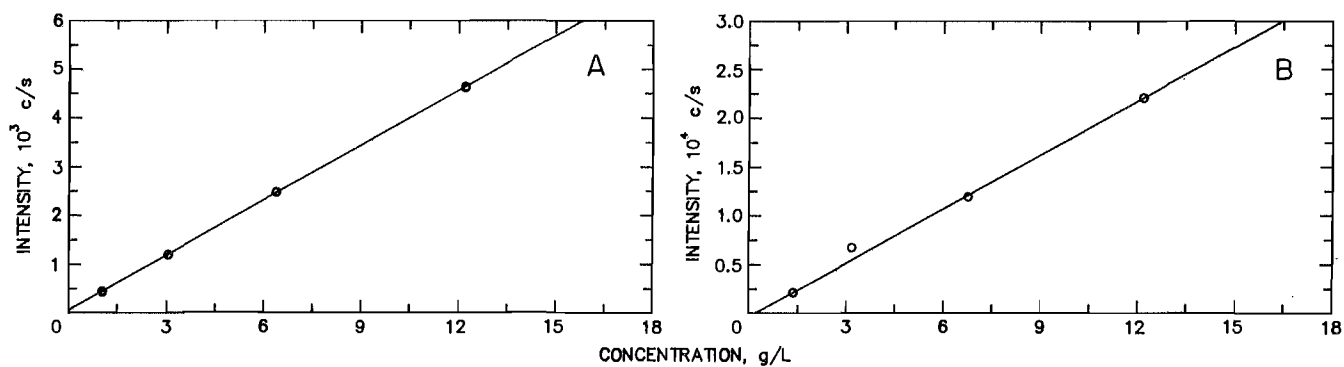


Figure 3.-Cobalt calibration curves. A, Thin film; B, bulk solution.

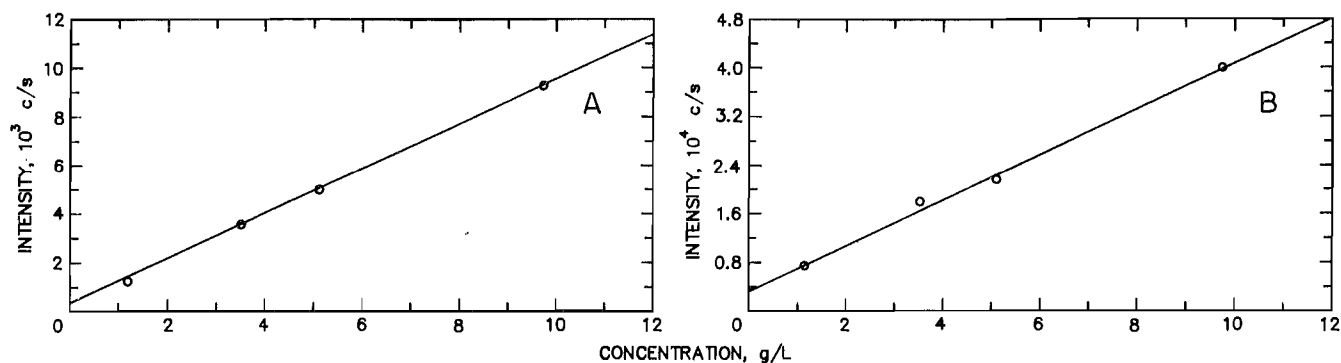


Figure 4.—Iron calibration curves. A, Thin film; B, bulk solution.

Figure 5 - 170 points

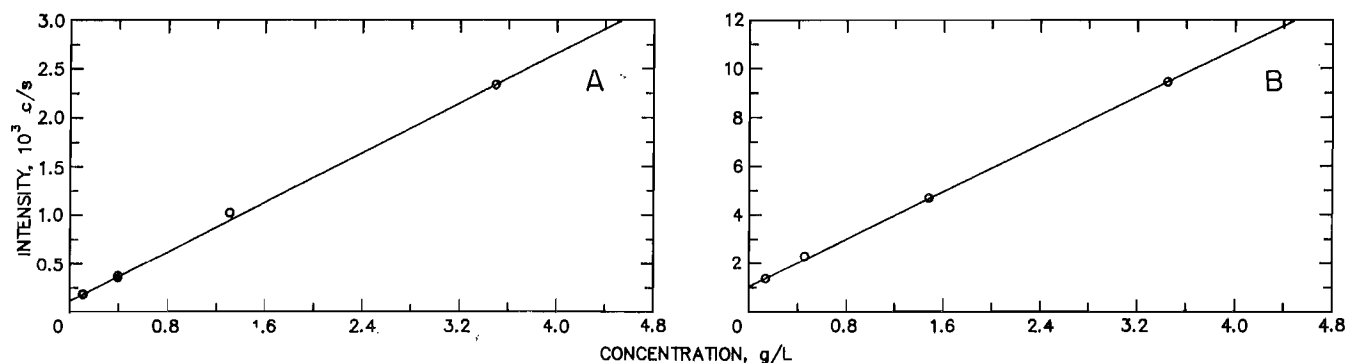


Figure 5.—Chromium calibration curves. A, Thin film; B, bulk solution.

RESULTS

The results of the analyses of the four test solutions are presented in table 3. All replicates of test solution 4 were analyzed consecutively on the same day, while replicates of test solutions 1, 2, and 3 were analyzed on various days. Statistical precision is not significantly different for the test solutions run on various days. One result, replicate 6 of test solution 4, was rejected and not included in the statistical treatment of the data. On the basis of Student's *t*-test, using a 99-pct confidence interval, it was determined that this result was not a member of the population.

The results of the analyses of the binary solutions are presented in table 4. Each result is the average of four determinations. In spite of the fact that Cu concentration ranged from 0 to almost 100 g/L, no enhancement of Co was detected. Analyzed concentrations for both Cu and Co in all solutions agree quite well with calculated concentrations, even though the analytes Ni, Fe, and Cr were present during the standardization but absent from these solutions. Also, the Cu concentration in binary solution 4 is twice that of the highest standard.

Table 3.—Results of analyses of test solutions, grams per liter

Replicate	Cu	Ni	Co	Fe	Cr	Cu	Ni	Co	Fe	Cr
Test Solution 1						Test Solution 2				
1	(¹)	28.67	6.94	(¹)	9.80	20.15	60.82	4.56	1.53	6.45
2	(¹)	28.83	6.95	(¹)	9.88	20.11	60.91	4.57	1.52	6.49
3	(¹)	28.62	6.94	(¹)	9.98	20.73	62.79	4.68	1.58	6.53
4	(¹)	28.36	6.84	(¹)	9.83	20.94	63.32	4.70	1.61	6.65
5	(¹)	28.31	6.86	(¹)	10.00	20.80	63.29	4.63	1.56	6.55
6	(¹)	28.52	6.91	(¹)	10.02	20.81	63.04	4.66	1.58	6.55
7	(¹)	28.57	6.93	(¹)	9.84	20.85	63.14	4.68	1.56	6.64
8	(¹)	28.58	6.92	(¹)	9.95	20.95	63.26	4.69	1.56	6.66
9	(¹)	28.47	6.92	(¹)	9.82	21.04	63.82	4.74	1.58	6.75
10	(¹)	28.16	6.86	(¹)	9.86	20.88	63.50	4.72	1.57	6.80
Av value	(¹)	28.51	6.91	(¹)	9.90	20.72	62.79	4.66	1.57	6.61
Acc value	(¹)	28.58	6.98	(¹)	9.76	20.42	61.69	4.70	1.50	6.54
Std dev	(¹)	.193	.039	(¹)	.082	.32	1.05	.060	.026	.113
CV	(¹)	.68	.56	(¹)	.84	1.59	1.67	1.28	1.65	1.73
EE	(¹)	.07	.07	(¹)	.14	.30	1.10	.04	.07	.07
Relative EE ..	(¹)	.24	1.00	(¹)	1.43	1.47	1.78	.79	4.67	1.07
Test Solution 3						Test Solution 4				
1	30.45	64.09	(¹)	2.27	(¹)	20.32	102.5	2.33	1.52	3.25
2	30.15	63.36	(¹)	2.25	(¹)	20.44	102.3	2.33	1.58	3.27
3	30.16	63.45	(¹)	2.22	(¹)	20.34	102.5	2.33	1.55	3.28
4	29.99	63.12	(¹)	2.19	(¹)	20.37	102.1	2.33	1.57	3.25
5	30.36	63.77	(¹)	2.23	(¹)	20.47	102.8	2.35	1.51	3.30
6	30.51	64.03	(¹)	2.25	(¹)	20.41	102.5	2.35	² 1.66	3.30
7	30.16	63.59	(¹)	2.19	(¹)	20.47	103.2	2.36	1.58	3.36
8	29.98	63.32	(¹)	2.20	(¹)	20.41	103.1	2.38	1.57	3.35
9	31.15	65.31	(¹)	2.30	(¹)	20.23	101.6	2.33	1.53	3.22
10	31.14	65.64	(¹)	2.26	(¹)	20.46	103.0	2.38	1.51	3.26
Av value	30.41	63.97	(¹)	2.24	(¹)	20.39	102.6	2.35	1.55	3.29
Acc value	30.61	63.95	(¹)	2.19	(¹)	20.41	102.1	2.38	1.48	3.28
Std dev428	.855	(¹)	.037	(¹)	.078	.490	.021	.030	.046
CV	1.41	1.34	(¹)	1.63	(¹)	.38	.48	.88	1.89	1.41
EE20	.02	(¹)	.05	(¹)	.02	.50	.03	.07	.01
Relative EE ..	.65	.03	(¹)	2.28	(¹)	.10	.49	1.26	4.73	.30

Acc Accepted.

CV Coefficient of variation.

EE Error of estimation.

¹Concentration below standard range.²Rejected on basis of Student's t-test.

Table 4.—Results of binary solution analyses, grams per liter

Solution	Analyte	Analyzed	Calculated
1	Cu	(¹)	0.0
	Co	10.23	10.00
2	Cu	24.35	24.36
	Co	10.14	10.00
3	Cu	51.69	51.33
	Co	10.19	10.00
4	Cu	98.80	99.82
	Co	10.05	10.00

¹Concentration too low for analysis.

DISCUSSION AND CONCLUSION

Thin-film specimen calibration curves for all elements demonstrate linear intensity versus concentration relationships. Calibration curves for bulk solutions with the exception of Cr did not demonstrate such relationships. The bulk solution calibration curve for Cr was linear because of the narrow concentration range of the standards. Another reason for its linearity may be the fact that the analyte Cr is subject only to enhancement effects, which are not as large as absorption effects. The results of the analysis of the four binary solutions agree well with calculated concentrations in spite of the wide Cu concentration range in these solutions. The results of the analysis of binary solution 4 indicate that the linear range for Cu is twice that of the standards. From these observations it is concluded that the method of sample preparation presented here results in specimens that possess thin-film properties. The most important of these properties, analyte intensity, which is substantially independent of matrix, is shown in calibration curves and analyses of test solutions and binary solutions.

Statistical treatment of data generated by the analysis of 10 replicates of each of 4 test solutions is presented in table 3. No coefficient of variation was found to be greater than 2 pct for any of the five analytes in any of the test solutions. Six of the sixteen coefficients of variation

were less than 1 pct. Similarly, with the exception of Fe, all relative errors of estimation were less than 2 pct: eight were less than 1 pct.

Iron showed a slightly larger error of estimation than the other analytes. The absolute error of estimation was small, ranging from 0.05 to 0.07 g/L. These figures are comparable to those of the other analytes; however, measurement of smaller amounts of Fe resulted in larger relative errors. These errors were not deemed excessive. During the initial stages of the development of this method, a systematic Fe background problem was noted. A filter paper blank was run with all available sample holders, and those with similar Fe backgrounds were used in all subsequent work. Similarly, Fe backgrounds were measured on a large number of sample cells, and several of those that exhibited similar Fe intensities were chosen to be used in further work.

It is concluded that the method presented here provides a precise and accurate way to determine the major constituents Cu, Ni, Co, Fe, and Cr in superalloy leach liquors. This method is significantly quicker and simpler than traditional wet chemical methods. Additionally, it does not suffer from the interelement effects encountered during XRF analysis for bulk materials of this nature.